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Empirical Background Calculation Method for Multi-Channel X-ray Spectrometers

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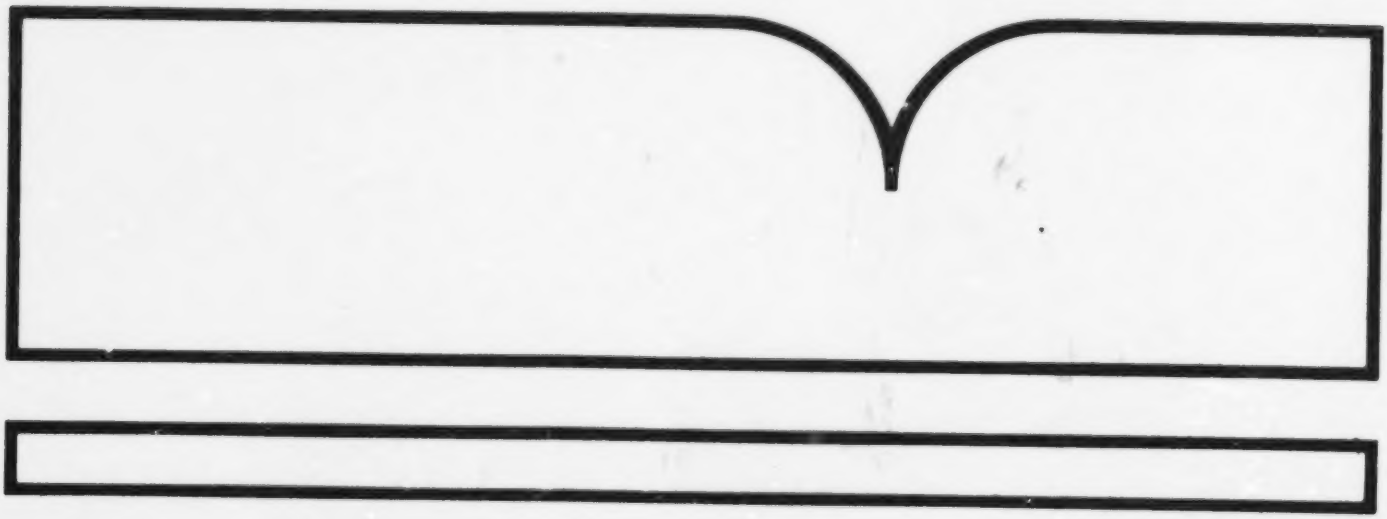

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AN EMPIRICAL BACKGROUND CALCULATION METHOD FOR MULTI-CHANNEL X-RAY SPECTROMETERS

by

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16. ABSTRACT

A method of background calculation has been developed which is applicable to fixed-channel wavelength-dispersive spectrometers which cannot directly measure background. The x-ray intensities from a set of high- and low-average atomic number standards are fitted against Rayleigh and Compton scatter parameters to an equation of the form: $y - a x_1 + b x_2 + c$. Y is the calculated intensity, x_1 and x_2 are Rayleigh and Compton scatter parameters, and c is a constant. Correlation coefficients greater than 0.99 and slopes of 1.00 are obtained for most elements measured. Calculated and measured backgrounds as well as concentrations are reported for selected standard reference materials.

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AN EMPIRICAL BACKGROUND CALCULATION METHOD FOR MULTI-CHANNEL X-RAY SPECTROMETERS

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INTRODUCTION

Several literature references[1-2] address the relationship between the reciprocal of the absorption coefficient and the Compton scatter peak intensity. Most workers use a Compton scattered tube line in the calculation of background; however, use of Bremsstrahlung scatter in the present work is also valid for this calculation. Background calculation for a fixed-angle monochromator is desirable since the background cannot be measured off peak. A method for calculating background for fixed-channel instruments by summing the calculated Rayleigh and Compton scatter intensities is presented in this paper.

THEORY AND ASSUMPTIONS

The Rayleigh and Compton scatter intensities from a flat homogeneous specimen of any thickness are given by[3]:

$$I_r = \frac{K_r I_o S_r}{\mu_2(\csc\Psi_1 + \csc\Psi_2)} [1 - EXP - \mu_2(\csc\Psi_1 + \csc\Psi_2)G] \quad (1)$$

$$I_c = \frac{K_c I_o S_c}{\mu_1\csc\Psi_1 + \mu_2\csc\Psi_2} [1 - EXP - (\mu_1\csc\Psi_1 + \mu_2\csc\Psi_2)G] \quad (2)$$

where

I_r, I_c = Rayleigh and Compton scatter intensities, respectively

K_r, K_c = overall efficiency constants,
I_o = incident intensity on the specimen,
G = surface density of specimen (g/cm^2),
μ_1, μ_2 = absorption coefficient for incident and scattered radiation, respectively (cm^2/g),
S_r, S_c = Rayleigh and Compton scatter coefficients, and
Ψ_1, Ψ_2 = incidence and take-off angles.

The composition-dependent portion of the Rayleigh and Compton scatter coefficients are given by[4]:

$$S_r = k_r \sum_i W_i z_i^3 / A_i \qquad (3)$$

$$S_c = k_c \sum_i W_i z_i / A_i \qquad (4)$$

where

W_i = the weight fraction of the i-th element in the specimen,
A_i, z_i = the atomic mass and atomic number, respectively,
k_r, k_c = constants containing the energy- and angular-dependent portion of the scatter coefficient.

Equation 2 is simplified for convenience by setting $\mu_1 = \mu_2$. This approximation is valid for environmental samples because of the unlikely nature of major element absorption edges lying between the Rayleigh and Compton wavelengths for the elements whose backgrounds are to be calculated (see Equipment Section). Incorporating this approximation into Equation 2, assuming infinite thickness and replacing S_r and S_c by Equations 3 and 4, respectively, yields an equation in the form of Equation 5 for the total scattered intensity or background:

$$I_{bkg} = A\ \sigma_r/\mu_2 + B\ \sigma_c/\mu_2 + C \qquad (5)$$

In Equation 5, the summation in Equations 3 and 4 was replaced by σ_r and σ_c; $K_r k_r I_o/(\csc\Psi_1 + \csc\Psi_2)$ was replaced by A; $K_c k_c I_o/(\csc\Psi_1 + \csc\Psi_2)$ was replaced by B; and C is a constant inserted to allow for a non-zero intercept due to background resulting from sources independent of the specimen matrix, such as scattering from both specimen and crystal holder. The absorption coefficient μ_2 is determined by the expression $\Sigma W_i \mu_{i,\lambda}$, where W_i is the weight fraction of element i and $\mu_{i,\lambda}$ is the absorption coefficient of element i for wavelength λ. The constants A, B, and C are determined by a multiple linear regression analysis of data collected on laboratory-prepared standards. These standards were chosen to represent a broad dynamic range of the scattering parameters σ_c/μ_2 and σ_r/μ_2.

EQUIPMENT

All measurements are made on a Siemens MRS-3 multi-channel spectrometer[5] equipped with fixed and scanning monochromators. The fixed-channel elements whose backgrounds are to be calculated are molybdenum (Mo), strontium (Sr), lead (Pb), and bromine (Br). The scanning monochromator is equipped with a sealed xenon proportional detector and has a scanning range of 11.700 keV (30.10 °2θ) to 3.52 keV (119.5 °2θ). All analyzing crystals are lithium fluoride (LiF_{100}). The K_α lines are used for all elements except for Pb where the L_β line is used. Excitation of the X-ray spectra is provided by a chromium (Cr) target tube operated at 54 kV constant potential and 44 mA for all measurements.

PREPARATION AND ANALYSIS OF STANDARD SCATTERING MATERIALS

Two sets of scattering standards are prepared to favor Rayleigh and Compton scatter, respectively. The Compton set (referred to as low z standards) consists of Fe_2O_3 in concentrations ranging from 90% to 7.5% in Carbowax 6000. The average z ranges from 11 to 3.6. The Rayleigh set (referred to as high z standards) consists of selected high-purity oxides or salts of elements of atomic numbers (z) ranging from 11 to 30. They are pressed either pure or with small (<10%) amounts of Carbowax 6000. The average z for these standards ranges from 8.4 to 18. All standards and samples are prepared greater than infinite thickness.

The intensity data for the high and low z standards are plotted in Figure 1 against their respective scatter parameters. This figure represents the experimental data graphically, and no functional relationship should be assumed between the observed intensity and the respective scatter parameters because the observed intensities have components of both Rayleigh and Compton scatter. However, the data do qualitatively illustrate the observed intensity as a function of the parameter most closely associated with the scattering process producing the intensity.

The coefficients A, B, and C in Equation 5 and their 95% confidence interval are determined by multiple linear regression analysis and are reported in Table 1. A plot of intensity measured at the analyte line position versus the calculated intensity is shown for Sr in Figure 2. All experimental data points are plotted, but data points with standardized residuals greater than two were rejected in the final determination of the regression coefficients. (See Discussion.)

Figure 1. Intensity of 14.14-keV X-rays (S_r).

EXPERIMENTAL RESULTS

Two related approaches were used to assess the applicability of the method. In the first approach, the intensities are measured on synthetic laboratory standards using combinations of the same high-purity materials used to prepare the scattering standards but with a different binder, boric acid. The combinations were chosen to give widely diverse compositions and are summarized in Table 2. In addition to synthetic standards, a standard reference material, SRM 120b (calcium phosphate rock), is also measured. This was chosen because a qualitative scan on a different spectrometer capable of scanning over the analyte lines of the elements of interest showed only Sr as an interfering element. The scatter parameters are calculated based on the certified concentrations from SRM 120b and the gravimetrically determined concentrations for the synthetic standards. The backgrounds are calculated using Equation 5 with the fitted coefficients from Table 1. A comparison of the measured and calculated count rates is given in Table 3.

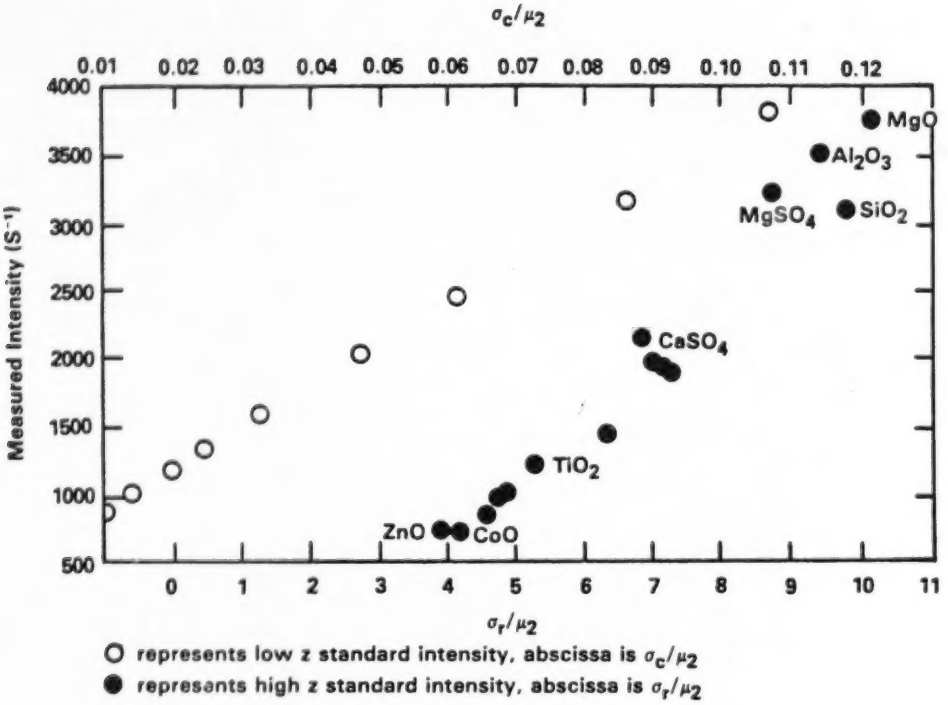

Figure 1. Intensity of 14.14 keV X-rays (Sr).

Table 1. Regression Coefficients

Figure 2. Correlation of measured and calculated intensities for 14.14-keV X-rays (S_r).

Table 1. Regression Coefficients

Element[a]	A	B	C	r[c]	Slope[c]	Intercept[c]
Mo	70 ± 19[b]	38865 ± 1009[b]	369 ± 164[b]	0.9995	1.000 ± 0.031	0 ± 66
Sr	165 ± 32	24774 ± 1709	-77 ± 146	0.9978	1.000 ± 0.016	0 ± 70
Pb	312 ± 52	46434 ± 2377	-27 ± 186	0.9984	1.000 ± 0.025	0 ± 81
Br	368 ± 44	58606 ± 1573	-148 ± 139	0.9996	1.000 ± 0.012	0 ± 47

[a]Some data points used in the determination of A, B, and C were deleted; see Discussion for details.
[b]Represents 95% confidence interval for coefficient.
[c]Correlation coefficient, slope, and intercept from Figure 2.

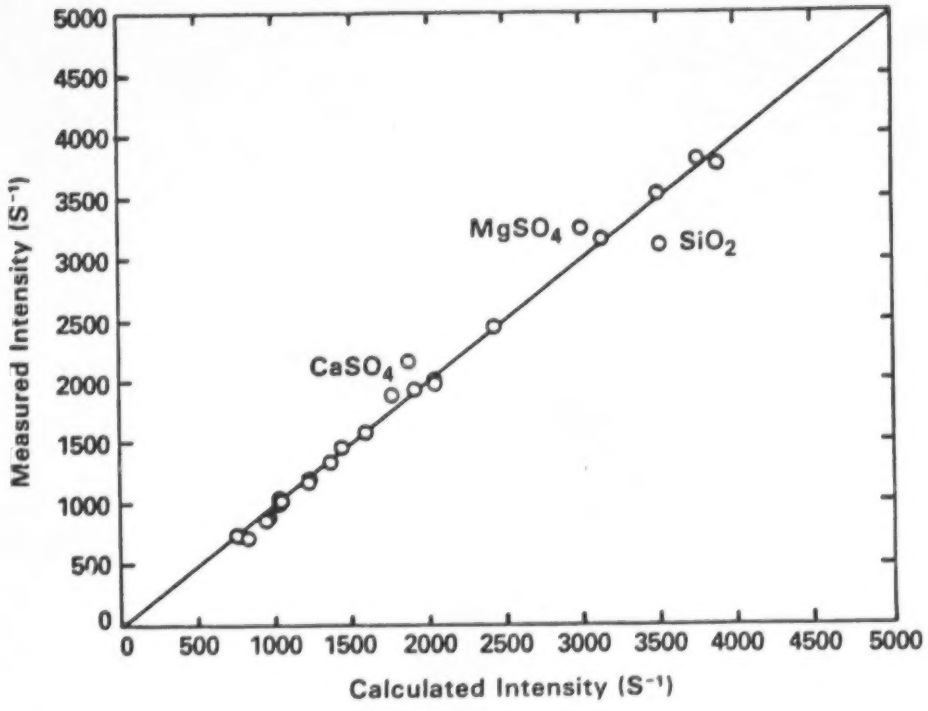

Figure 2. Correlation of measured and calculated intensities for 14.14 keV X-rays (Sr).

Table 2. Weight Fraction of Components of Synthetic Standards

The second approach to judge the method involves the X-ray fluorescence analysis of SRM 1633A (coal fly ash). In the background calculation on unknown samples, the weight fractions of all elements used to determine the absorption and scatter coefficients are determined by iteration. Major non-analyzable elements, such as oxygen in fly ash, are determined by difference, assuming that the sum of weight fractions equals unity. Table 4 shows the analysis results. Four elements analyzable on the scanning channel are also included in the data as an additional check on the method. Due to the lack of standard reference materials with concentrations sufficiently high (>100 to 200 ppm) for the elements under study, calculated and measured (where possible) backgrounds are reported as well as the concentrations.

Table 3. Intensities (s^{-1})[a] from SRM 120b (Phosphate Rock) and Synthetic Standards in Table 2

Table 2. Weight Fraction of Components of Synthetic Standards

Std	MgO	NaCl	S	Fe_2O_3	ZnO	KNO_3	H_3BO_3	Surface Density (g/cm^2)	Average z
1	0	0	0.484	0	0.516	0	0	0.448	17.4
2	0.0878	0	0.435	0.477	0	0	0	0.491	14.8
3	0.0236	0.0810	0.0837	0.0347	0.0383	0.0397	0.699	0.475	5.67

Table 3. Intensities (s^{-1})a from SRM 120b (phosphate rock) and Synthetic Standards in Table 2

Element	Std #1		Std #2		Std #3		SRM 120b	
	Calc	Meas	Calc	Meas	Calc	Meas	Calc	Meas
Mo	1621 ± 336b	1612	2170 ± 374	2268	5112 ± 493	5068	5824 ± 541	5748
Sr	878 ± 302	959	1159 ± 338	1258	2313 ± 443	2345	2610 ± 480	5389
Pb	1304 ± 373	1382	1687 ± 414	1815	3277 ± 531	3294	3647 ± 569	3491
Br	1249 ± 274	1327	1663 ± 303	1774	3395 ± 378	3303	3778 ± 403	3698

[a]All intensities measured at analyte line position.
[b]Represents 95% confidence interval of calculated intensity. All counting times are 100 s.

Table 4. Trace Element Analysis of SRM 1633A[a]

DISCUSSION

This technique has proven to be an acceptable approach to calculate background under the conditions described in this paper. The lower limit of applicability appears to be in the vicinity of 200 ppm and is due to the fairly broad range of the 95% confidence interval on the parameters in Table 1. However, the technique represents a solution to a heretofore unaddressed problem.

The points that deviate most from the straight line in Figure 2 are those observations made on the high atomic number standards. This deviation is expected from the data in Figure 1, which shows considerable scatter from the high z standards, possibly due to diffraction,[1] whereas diffraction effects are apparently absent in the low z standard data. There is a strong systematic bias in the SiO_2 data points, all of which had standardized residuals greater than two and were thus deleted from the data. The scatter SiO_2 was the only material that had to be ground before pressing; therefore, it could have been contaminated in the grinding process. The $MgSO_4$ data point was deleted from the Mo and Br data, and the $CaSO_4$ data point was deleted from the Sr data because their standardized residuals were also greater than

Table 4. Trace Element Analysis of SRM 1633A[a]

Element	Certified Conc (ppm)	Peak Count Rate (s^{-1})[b]	Measured Background[c] (s^{-1})	Conc[d] (ppm)	Calculated Background (s^{-1})	Conc[e] (ppm)
Mo	29	5375	NA[f]	NA	5116 ± 504[g]	34 ± 67[h]
Sr	830	6583	NA	NA	2393 ± 459	854 ± 103
Pb	72.4	3425	NA	NA	3334 ± 545	27 ± 162
Br	-	3477	NA	NA	3511 ± 384	ND(-9)[i]
Se	10.3	694.7	677.2	ND(4)	697 ± 158	ND(-1)
Bi	-	606.9	602.3	ND(3)	600 ± 128	ND(5)
As	145	1139	535.1	179 ± 11	541 ± 222	181 ± 73
Hg	0.16	452.9	449.3	ND(-3)	435 ± 226	ND(11)

[a]Conversion of intensities to concentration is accomplished by fundamental parameters technique.
[b]Counting times for Mo, Sr, Pb, and Br are 100 s; those for Se, Bi, As, and Hg are 20 s.
[c]Measured off peak.
[d]Concentration is based on measured background.
[e]Concentration is based on calculated background.
[f]Not applicable because background cannot be measured.
[g]Error figure represents 95% confidence interval of background uncertainty.
[h]Error figure represents 95% confidence interval of all random error sources.
[i]Element not detected. The figure in parentheses is the calculated concentration and indicates the concentration resulting from the difference in the peak count rate and the background.

two. Moisture absorption by these latter two compounds during preparation would lower the average z, thus producing higher intensity, as observed, but no efforts were made to verify this effect.

The measured intensities in Table 3 agree better than the 95% confidence band predicts, except for Sr in SRM 120b, which is due to an uncertified concentration of Sr in the sample. The overall agreement is quite good. Except for the Sr contaminant, the calculated values are well within 10% of the measured value for all measurements.

Table 4 presents information similar to that in Table 3 with the important addition of the calculated concentration and the 95% confidence interval. Almost all of the uncertainty in the concentration is due to the uncertainty in the calculated background. The magnitudes of the uncertainties are consistent with the interpretation that the lower limit of the method is in the vicinity of 200 ppm.

This method is being extended to aerosol-loaded filters and other samples less than infinitely thick.

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